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TROPOSPHERIC HO DETERMINATION BY FAGE

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In the detection of tropospheric HO by laser-excited fluorescence, we have introduced an alternative air-sampling method, named FAGE (Fluorescence Assay with Gas Expansion). Here the air is expanded through a nozzle (to 10^{-2}–10^{-3} atm) prior to excitation, in order to improve the ratio of the HO signal to the scattered, fluorescent, and photolytic backgrounds. The improvement comes from the differing pressure dependence of the intensities of these four terms, as well as the distinguishability of their temporal waveforms at low pressures when excited by a pulsed laser.

In this work, HO has been excited by a YAG/dye laser via the A,1 <-- X,0 $Q_1$1,1' transitions at 282 nm, with fluorescence detection in the A,0 -->, X,0 band near 309 nm. Other lasers and pumping paths may perform as well or better in this method. We have determined HO in urban air, where all three background terms are larger than in the remote troposphere.

With FAGE, chemical modulation of the HO signal has been achieved by hydrocarbon addition to the nozzle flow, converting photolytic HO from an interference to a background. Chemical calibration of the instrumental response to external HO has also been achieved, by hydrocarbon decay, at HO concentrations within the ambient range.

The method and the instrument have been described in Reference 1. Since then, FAGE sensitivity to ambient HO has been improved by a higher rep-rate, higher pulse-energy laser; narrow-band interference filters with f/1.5 collectors; and two parallel air-sampling channels. A steady-state modification of the hydrocarbon-decay method has allowed multipoint FAGE calibration throughout the NO-NO_2-O_3 progression.

Reference 1:

T.M. Hard, R.J. O'Brien, C.Y. Chan and A.A. Mehrabzadeh, Environmental Science and Technology 18 768-777 (1984).

Comments

These authors claim a 10 percent absolute accuracy using their method of sampling from a Teflon bag containing OH and other species. In the future, with optimization of the pressure reduction nozzle and time gating, they expect to measure $2 \times 10^5/cm^3$, with a signal-to-noise level of 2 and an absolute accuracy within a factor of 2.

The OH level in the bag is calibrated by the time decay of hydrocarbons and the FAGE technique by sampling from the bag. Questions were raised concerning wall effects, but these only occur near the end of collapse of the bag. The probe is moved around within the bag itself. The photochemical conditions which produce the OH are varied; these are concentrations of O_3, H_2O, NO and hydrocarbon, and the ultraviolet intensity. What are the effects from unsaturated compounds, which have a pressure and temperature dependent rate constant? Altogether, considerable concern was voiced by the workshop participants about the calibration method; while there were no obvious problems, it was felt that a study of the method was warranted.

This method appears ready to move into a ground-based collaborative effort together with the long-path absorption. Consideration has not yet been given to aircraft operation and special problems which could occur there, for example, H_2O clustering at 220K for flights higher in the troposphere.

This method can be combined directly with a determination of HO_2 by chemical conversion as described below. This combination has decided appeal for measurements of the ratio $[OH]/[HO_2]$ which appears of special interest as a test of the models.